National Bureau of Standards

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Light Wave of Mercury 198 as Ultimate Standard of Length

A new and better standard of length now exists in the wavelength of green radiation of mercury 198, an isotope transmuted from gold by neutron bombardment. In precision, reproducibility, and convenience, the new standard is superior to both the standard meter and the red line of cadmium, according to recent investigations by Dr. William F. Meggers of the Bureau's Atomic Physics Division. Preliminary measurements by Dr. Meggers have shown an accuracy of one part in a hundred million of relative values, and one part in a billion is theoretically possible.

Since 1889 the world's standard of length has been the "meter" distance between two lines on a platinum-iridium bar at the International Bureau of Weights and Measures in France. Fundamental measurements throughout all of science and industry are based on this standard, but it has several disadvantages. First, line standards are unsuitable in certain fields of measurement. Second, the intrinsic nature of lines ruled on surfaces—such lines are in effect small furrows—limits the precision attainable. Third, the meter is not readily reproducible.

Primarily because the standard meter does not afford sufficient precision in some fields, the red line of cadmium has been universally used for many years for precise measurements. However, the cadmium standard also has serious disadvantages. First, there is a fine structure in the red radiation that prevents the line from being as sharp as desirable and thus limits the precision possible. Second, the cadmium standard requires excitation in a furnace, and this entails unwanted broadening of the spectral line because of relatively high temperature.

The green line of mercury 198 has none of the disadvantages of either the meter or the red line of cadmium. The normal human eye, for example, is far more sensitive to green than to red, an important consideration in visual adjustment of the interferometer with which lengths are measured and compared. All other characteristics desirable in a light-wave standard—such as ability to be reproduced, absolute sharpness of the wavelength, intensity of the spectral line, life, and convenience of maintenance—are possessed to a greater extent by mercury 198.

The future refinement of physical optics—for example, an accurate determination of the velocity of light—and the improvement of mechanical processes—for example, the ruling of better diffraction gratings—are dependent on the production and adoption of an ultimate standard of length superior both to the meter bar and to the wavelength of red radiation from cadmium. The nuclear reaction that now makes possible large-scale transmutation and manufacture of pure elements not found in nature will also produce

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any desired quantity of the pure mercury from gold, and thus provide a material for a spectroscopic light source that emits light waves much more monochromatic than any emitted by natural elements. Theoretically, mercury isotope 198 should show interference patterns with retardations exceeding a million waves, and because it is possible with monochromatic lines to measure one one-thousandth of a wave, it is probable that the relative value of Hg^{198} wavelengths may eventually be determined with an accuracy of one part in a billion.

As long ago as 1927, the National Bureau of Standards recommended that the International Conference of Weights and Measures adopt a light wavelength, that of red radiation from cadmium vapor, as the primary standard of wavelength, and that the meter be defined in terms of this wavelength. The Conference objected that such a definition of the meter would menace the metric system, and explained that it was not a question of giving a true relation between the meter and the wavelength, but only a metric value of the latter which could be modified by future experiments. Strictly speaking, the world's primary standard of length is still the distance between two relatively wide lines drawn on a metal bar, despite the fact that practically all precise measurements of lengths in the Twentieth century have been made, and will continue to be made, with light waves.

The most monochromatic spectral lines are emitted by massive slow-moving atoms, and because mercury atoms are nearly twice as heavy as cadmium atoms and can be excited to radiate at less than half the absolute temperature, mercury lines are less than half as wide as cadmium lines, other things being equal. Wavelengths from natural mercury cannot be used as standards of length because natural mercury consists of a fixed mixture of seven isotopes with atomic masses of 196, 198, 199, 200, 201, 202, and 204, and each isotope emits one or more spectral components, none of which are exactly coincident. Consequently, the green line of natural mercury has sixteen components.

Transmutation of Gold to Mercury

Because the effective wavelength of such a complex line observed interferentially varies with the phase relations of the various components, it is imperative to avoid complex lines in selecting a natural standard of length. This objectionable feature of mercury lines could be removed if a single isotope, for example Hg^{204}, could be separated from the rest, but up to the present it has not been practicable to isolate an isotope of natural mercury in sufficient quantity to make satisfactory lamps. However, this goal has now been achieved by transmuting gold (Au^{197}) into Hg^{198}. The feasibility of doing this was first demonstrated in 1940 by J. Wiens and L. W. Alvarez, who reported that bombardment of gold by neutrons from a 60-inch cyclotron at the University of California produced enough mercury to be detected spectroscopically.

In 1942, the National Bureau of Standards purchased 40 ounces of proof gold, and enlisted the cooperation of the University of California to expose this gold to neutrons for one or more years. Unfortunately, World War II interrupted the experiment and only submicroscopic quantities of artificial mercury were made. The prospects were very discouraging until, near the end of the war, there were rumors of a secret source of neutrons thousands of times more effective than the largest cyclotron. In 1945, the National Bureau of Standards gold was transferred from California to Tennessee. The treatment this gold received was not disclosed, but a year later the Bureau distilled from it about 60 milligrams of mercury, which was found from spectroscopic tests by Dr. Meggers, chief of the Bureau's Spectroscopy Section, to be pure Hg^{198}. In anticipation of a considerable demand for Hg^{198}, the Atomic Energy Commission has been requested to bombard more gold with neutrons to produce one or more grams of Hg^{198} within a year. In the meantime, the available Hg^{198} has been used by Dr. Meggers in the preparation of several types of lamps which are being studied to determine which will be most suitable as a standard.

In the design of a Hg^{198} lamp that will emit radiations suitable as ultimate standards of length, a maximum is desirable in each of the following five characteristics: (1) Monochromaticity, (2) reproducibility, (3) intensity, (4) life, and (5) convenience. It is perhaps obvious that some of these requirements conflict with others, and that it will be necessary to make compromises. It appears probable that either

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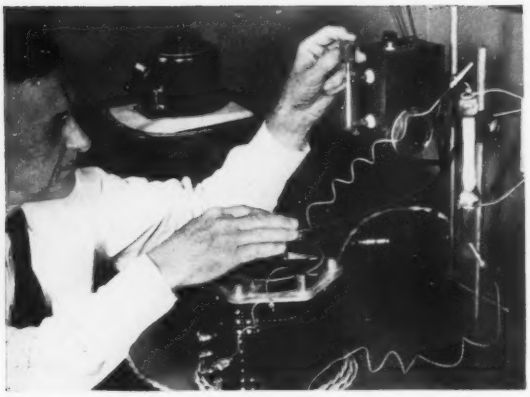
The wavelength of green radiation of mercury 198, an isotope transmuted from gold by neutron bombardment, offers a new and superior standard of length. (Top) In the optical train used at the Bureau for obtaining values of the wavelengths of mercury 198, light from the electrodeless mercury lamp (*A*) (excited by high-frequency radio waves) and from the cadmium lamp (*B*) passes simultaneously through a Fabry-Perot interferometer (*C*) into a prism spectrograph (*D*) where interference patterns of each line are photographed. (Lower) Relative values of wavelengths are derived from measurements of the Fabry-Perot interference patterns.



Relative values of the wavelengths of mercury isotope 198, accurate to one part in a hundred million, have been obtained, from preliminary measurements, using an electrodeless lamp (left) operated with radio waves. The reference cadmium lamp (right) is operated by 60-cycle alternating current.

electrodeless tubes or Geissler tubes (similar to the ubiquitous luminous signs), containing several milligrams of Hg^{198} and a small amount of argon gas, will be useful for accurate measurements.

Employing an electrodeless lamp excited by high-frequency radio waves, preliminary values of the wavelengths of a dozen Hg^{198} lines, ranging from the ultraviolet (3,341 A) to the yellow (5,791 A), have been measured by Dr. Meggers. Though publication of the observed wavelengths of Hg^{198} will be deferred until final values are in hand, these preliminary values, when tested by the combination principle of spectroscopy, appear to be correct within one part in one hundred million, whereas the best measurements made with natural mercury exhibit deviations of one part in one hundred thousand, due, no doubt, to the falsification of the wavelengths by the complexity of the lines.

Although cadmium and mercury are divalent chemical analogues, and therefore exhibit relatively simple and similar atomic spectra, whatever differences exist are invariably in favor of mercury. For example, the brightest line in the cadmium spectrum occurs in the blue-green (5,086 A), whereas the mercury analogue is in the green (5,461 A) nearly coincident with the maximum sensitivity of the normal human eye. The red wave of cadmium (6,438 A) is intrinsically only one-tenth as intense as the strongest line (5,086 A), and is further handicapped by the fact that the eye is only one-seventh as sensitive for red as for green. Thus for the visual adjustment of interferometers, the green line of mercury is seventy times as intense as the red line of cadmium. The mercury analogue of the cadmium red line is a yellow line (5,791 A), which is always accompanied by another yellow line of shorter wavelength (5,770 A) but nearly equal intensity. This yellow pair of mercury lines produces interference coincidences at intervals of 275 waves, and is happily heuristic for the whole order of interference without counting any fringes; it has no convenient counterpart in cadmium.

Mercury is the only heavy stable element that has an appreciable vapor pressure below zero degrees centigrade, and therefore is unique among all elements in radiating, at low pressure and temperature, a relatively simple spectrum of extremely sharp lines provided isotopic structure is eliminated. The green line of mercury, rejected by Michelson 55 years ago on account of complex structure, has finally, by the production of mercury 198, been freed of its seven-isotope curse, and the green line of Hg^{198} now stands alone as the most nearly ideal standard wavelength that can ever be obtained from any atoms, natural or artificial. Coupled with the fact that adequate quantities of absolutely pure Hg^{198} may now be obtained by neutron bombardment of gold in chain-reacting piles, the unique properties of Hg^{198} force the conclusion that a progressive scientific world will eventually adopt the wavelength of green radiation (5.461 A) from Hg^{198} as the ultimate standard of length.

Light-Wave Standards

The meter unit, the present unit of length, was created about 1790 to represent one ten-millionth of the earth's quadrant. In 1827, some natural philosophers meeting in Paris agreed that the meter could not be reproduced if the form of the earth were changed by collision with a comet. A Frenchman, Jacques Babinet, then proposed a light wave in a vacuum as a natural unit of length independent of the earth's dimensions. Later the same thought was expressed by German, Dutch, and British scientists, but the first practical results must be credited to Americans, A. A. Michelson and E. W. Morley, who, in 1887, outlined "A method of making the wavelength of sodium light the actual and practical standard of length." Their method, involving the use of the optical interferometer devised by them for their celebrated experiments on the relative motion of earth and ether, consisted of the measurement of a length and the counting of an equivalent number of interference fringes.

In 1889, Michelson and Morley described in detail a method of measuring the meter in light waves, and predicted that the brilliant mercury green line would in all probability be the wave to be used as the ultimate standard of length. Searching systematically for the radiation best suited as an ultimate standard, Michelson discovered in 1892 that the green light of mercury is complex, and discarded it in favor of the red light of cadmium. These classic investigations promptly led to Michelson's invitation to the International Bureau of Weights and Measures, where he performed his celebrated determination of the relation between the meter and the wavelength of cadmium red radiation. In the succeeding 40 years, Michelson's experiment was repeated a half-dozen times and his result has been amply confirmed, considering the fact that the lines on the meter bar are ten to twelve wavelengths wide.

Indeed, it is the character of ruled lines themselves which limits the accuracy of wavelength-meter intercomparisons, and there is therefore hardly any point to measuring the wavelengths of Hg^{198} lines relative to the meter. The wavelength of Hg^{198} green light can readily be measured relative to cadmium red light from ten to one hundred times more accurately than either can be measured relative to the meter. Adoption of the present provisional relation as exact, and subsequent substitution of Hg^{198} green for cadmium red appears to be the logical and expeditious approach to a better standard of length.

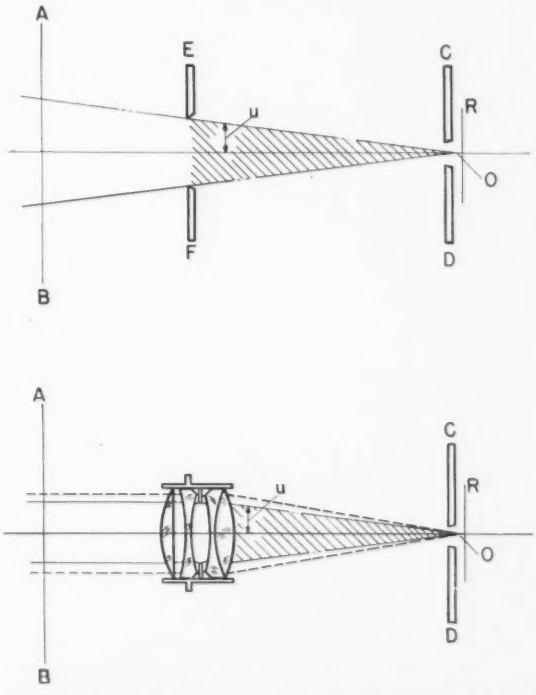
Calibration System for Photographic Lenses

An improved system for calibrating the diaphragm openings of a photographic lens,[1] developed by Dr. Irvine C. Gardner of the Bureau's optical instruments laboratory, permits a more precise and accurate control of the amount of light admitted to a photographic film during an exposure. This method of calibrating and marking apertures, in contrast to the system that has been in use, takes into account the losses of light from absorption, reflection, and scattering within the lens. Increased uniformity and quality of product result. Such a system of marking is particularly important in color photography because of the smaller latitude of exposure of color film.

Until a few years ago, photography was largely an empirical art, and each photographer's practice was based on his experience with his own particular equipment. Now, however, the principles underlying photographic work are so well known, and quantitative relations so well established, that photographic engineering has become an applied science. This change has been greatly stimulated by the savings and improvement in technical quality resulting from advances in photographic technique, particularly in the motion picture industry, where large quantities of expensive film must be exposed. Meanwhile, the development of the modern photoelectric exposure meter and the more general dissemination of quantitative information regarding the properties of emulsions have made it possible, not only for the professional, but also for the skilled amateur, to control his results in a scientific manner.

With this progress a demand has arisen for the extension of similar precision to the speed marking of lenses. The method now in general use is based entirely upon the ratio of the equivalent focal length of the lens to the diameter of the aperture. This ratio—known as the *f*-number—gives no consideration to the great differences in the useful light transmitted by various lenses. These differences are the result of absorption in the glasses of which the lens elements are made, or reflection and scattering at the surfaces. The introduction of reflection-reducing coatings has accentuated this variation in performance to such an extent that for a given *f*-number the light transmitted by two lenses may differ almost by a factor of 2.

In the method of calibration developed at the Bureau, the marking "8," for example, does not correspond to the geometrically determined aperture ratio 1:8, but to an opening sufficiently large to permit the transmission of as much light as would be transmitted by a lens set at the aperture 1:8 if there were no losses. Such a system of apertures may be referred to as equivalent or compensated apertures. The markings are obtained by a relatively simple photometric procedure, in which the diaphragm of the lens to be calibrated is adjusted to transmit the same amount of light as a similarly placed opening of standard size. This standard opening corresponds to an ideal lens of a given aperture ratio, in which incident light is wholly trans-



A new system developed at the Bureau for calibrating photographic lenses is based essentially on a matching of two photometer readings. *AB* represents a uniformly bright surface, *CD* a metal plate with a small circular opening at *O*, and *R* a photocell receiver. The circular opening in plate *EF* is constructed so that in light transmission it is equivalent to an ideal lens with the aperture set at a designated opening, for example, *f*–4 (sine u=⅛). Replacing *EF* with an actual lens (lower) and adjusting the diaphragm (dash lines) until the readings match those for *EF* gives the corresponding *effective-f-number*. Similar values for other settings may be obtained by inserting plates at *EF* having openings of the proper sizes.

[1] For further technical details, see Compensation of the aperture ratio markings of a photographic lens for absorption, reflection, and vignetting losses, I. C. Gardner, J. Research NBS **38**, 643 (1947) RP1803.

mitted. A complete calibration is obtained for a given lens by the use of a series of openings of graduated size corresponding to various aperture ratio values. A standard designation for the new system of markings has not yet been agreed upon. Terms that have been suggested are *effective-f-number* and *t-number* (*t* standing for transmission).

The usefulness of this method of calibration is evident to the photographer. For example, a lens of large relative aperture and no coating may have eight surfaces, in which case the transmission of the lens may be as low as 66 percent. Yet a lens with low-reflection coatings and few surfaces may transmit 98 percent of the incident light. If exposures are made with the two lenses for the same length of time and at the same *f*-number (according to the system now in general use), the effective exposure with the one lens will actually be 50 percent greater than with the other. On the other hand, if the diaphragms are marked according to the proposed system, the exposures made at the same diaphragm settings for the two lenses will be identical. Except for the newer lens markings, this system requires no instrumental changes, and the process of determining the exposure time is no more complicated than that followed at present.

This calibration procedure is based on the illumination at the center of the field only. It thus insures equivalent exposures at the center of the image for lenses used at the same effective-*f*-numbers. However, it does not distinguish between the behaviors of different lenses that arise because of differences in vignetting, that is, the decrease of illumination at an off-center point due to restrictive action of parts of the lens elements or lens mount. Where vignetting must be taken into account, a similar procedure is followed, but, instead of measuring the illumination of a small area near the axis, the average light flux over the entire field is measured.

The method, as described, assumes that the object to be photographed is at an "infinite" distance and that the image will thus lie in the focal plane of the lens. This is the basis on which the markings now in use are engraved on the lens mounts, and it is entirely satisfactory for a large amount of photographic work. However, lenses for copy purposes, as well as some other types, are usually placed only a few focal lengths away from the object. In such instances it is highly desirable that the aperture ratios be marked for one or more selected object distances approximating those actually to be employed in practice. The new method of stop calibration can be readily extended to apply to this problem by suitably arranging relative positions of the lens and plates.

This system of lens calibration, involving only a matching of two photometer readings, is simple, direct, and accurate. As each calibration is essentially a substitution procedure in which the two values of brightness to be measured are of approximately the same value, errors arising from nonlinearity of response of the photometric apparatus are largely eliminated. The need for carefully calibrated filters is also avoided. Finally, the method provides a means by which different laboratories may arrive at the same calibration values without the interchange of physical standards, as apertures in metal plates—the only standards required—are readily constructed to the required sizes.

Standardization of the pH Scale

The pH unit, used to express numerically the degree of acidity or alkalinity of aqueous solutions, may be defined in a number of ways, each resulting in a slightly different value for the pH of a given solution. Consequently, several pH scales, based upon various definitions, have met with equal favor among chemists. In view of the increasing need in science and industry for accurate determinations of acidity, the National Bureau of Standards is recommending the universal adoption of a single standard pH scale, analogous to the International Temperature Scale. It is proposed that the pH assigned to solutions of buffer substances distributed by the Bureau as Standard Samples be taken as the fixed points on this standard scale.

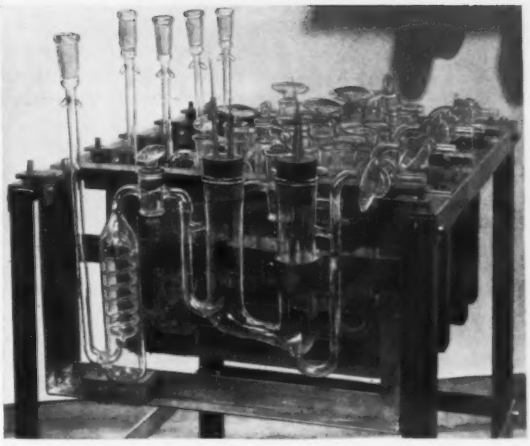
In the preparation of many commercial products—for example, paper, textiles, dyes, ceramics, and beer—the rapidity and efficiency of the processes depend upon accurate control of the acidity or alkalinity of aqueous solutions. Such control is now a regulatory requirement in the preparation of certain medicines and in the manufacture of paper and leather for the Government. In sugar manufacture, the inversion of sucrose can be regulated at will or avoided entirely by holding the acidity within certain limits. Similarly, regulation of the acidity of electroplating solutions permits the character of the deposit to be controlled. Another application of particular importance is the avoidance of corrosion and embrittlement of boiler walls and tubes by regulation of the acidity of boiler water. The widespread losses due to underground corrosion are likewise effectively curbed in many cases by proper adjustment of acidity.

The several convenient pH meters now available commercially enable precise determinations of pH values in such varied media to be made with ease and rapidity, but these values are based upon a scale fixed by the pH assigned to the standards with which the instrument has been calibrated. The differences among scales of pH are the direct result of different procedures, definitions, and assumptions employed in arriving at the pH of the standard. The pH may be defined in one instance as the negative logarithm of the hydrogen-ion concentration or, again, of the effective concentration or "activity" of this ion. Often the pH value as defined by Sorensen in terms of the electromotive force of a galvanic cell with hydrogen and calomel electrodes is chosen. Although the differences among these scales rarely exceed 0.1 unit, the need for greater accuracy makes desirable the general adoption of a single series of consistent pH standards.

In an effort to encourage standard procedure in pH measurements, the National Bureau of Standards is now supplying four buffer materials in the form of Standard Samples of certified purity. These substances are acid potassium phthalate, potassium dihydrogen phosphate and disodium hydrogen phosphate (intended to be used together), and borax. They are being distributed at the rate of several hundred samples annually. The certificates furnished with these compounds specify the pH of certain aqueous solutions of the sample, which can provide fixed points on a pH scale.

In order to assign exact values to these fixed points, it was necessary to set up a scale based upon some suitable definition of pH. A consideration of the advantages and limitations of several scales led to a choice of a modified activity scale as most convenient and practical for general use. Although the activity of a single ionic species can be simply defined only in very dilute solutions, the influence of the hydrogen-ion activity in chemical equilibria is of far-reaching importance.

The pH of the NBS standards is derived from measurement of the electromotive force of cells without liquid junction, in which they are used as electrolytes. These cells are specially designed, utilizing the highly reproducible hydrogen and silver-silver chloride electrodes. Computation of pH is based upon several reasonable assumed relationships between ionic activities and mean activities. These assumptions are found to give identical values for dilute solutions. The scale thus obtained approaches a true scale of activity for solutions of low concentration; at higher ionic strengths it is best regarded as a consistent scale that necessarily rests upon an assumption not subject to experimental proof.



Specially designed glass cells with highly reproducible hydrogen and silver-silver chloride electrodes are used for the accurate determination of pH of solutions of the standard pH samples issued by the Bureau.

Automotive Research

Large-scale synthesis and isolation of hydrocarbons by the Bureau's automotive laboratory have been factors in making available combat aviation gasolines of much higher knock rating than isooctane, a standard reference fuel on which the octane knock rating scale is based. This research, which is now being directed toward obtaining information on the combustion characteristics of jet fuel components, has produced scores of compounds, many hitherto unknown, in unsurpassed purity. In fuel quality some of these compounds—notably "tetrane," which was first prepared and named at the Bureau—far surpass even the much publicized triptane.

As the octane number scale is now inadequate to express the knock rating of many of the new aviation gasolines, the Bureau, in conjunction with the Cooperative Fuel Research Committee, has developed a "Detonation Index" scale designed to express knock ratings in the form most useful to the consumer. This scale is based on a reference fuel system composed of normal heptane and triptane, both containing tetraethyl lead, and can be extended indefinitely to apply to the higher-rating aviation fuels that may be produced in the future.

The development of fuel test methods; the calibration of reference fuels for knock testing; the synthesis of high-quality aviation gasolines; the study of substitute motor fuels, gasoline economizers, and antifreezes; and the testing of internal combustion engines of all types are representative projects indicative of the scope of the work of the Bureau's automotive laboratory. This group was organized as a result of the great need for automotive research which arose in the first World War. The more pressing problems then concerned aircraft, and much of the work of the new section was devoted to research on aircraft engines and gasolines. At this time the first altitude laboratory was designed, built, and put into operation. The fundamentals of aircraft engine and fuel performance under conditions matching exactly the thin air and extreme cold existing at altitudes up to 7 miles were established in this laboratory, the design of which was later copied by several other nations.

With the advent of peace, emphasis was placed on problems arising in the automotive and petroleum industries. Recognizing the need for common effort in the mutual adaptation of engines and fuels, the National Bureau of Standards joined with these industries in organizing the Cooperative Fuel Research (CFR) Committee in 1921. This Committee has been of immeasurable value in the development of motor vehicles and fuels in this country to their present high standards, unequalled elsewhere in the world.

One of the important phases of this cooperative work has been the development, standardization, and improvement of methods for testing motor, aviation,

and Diesel fuels. Twenty years ago, there was no uniform or accepted method for measuring knock ratings. Isooctane (2,2,4-trimethylpentane), the basis of the present octane number scale and a major constituent of the one-half billion barrels of aviation gasoline used in World War II, was then unknown.

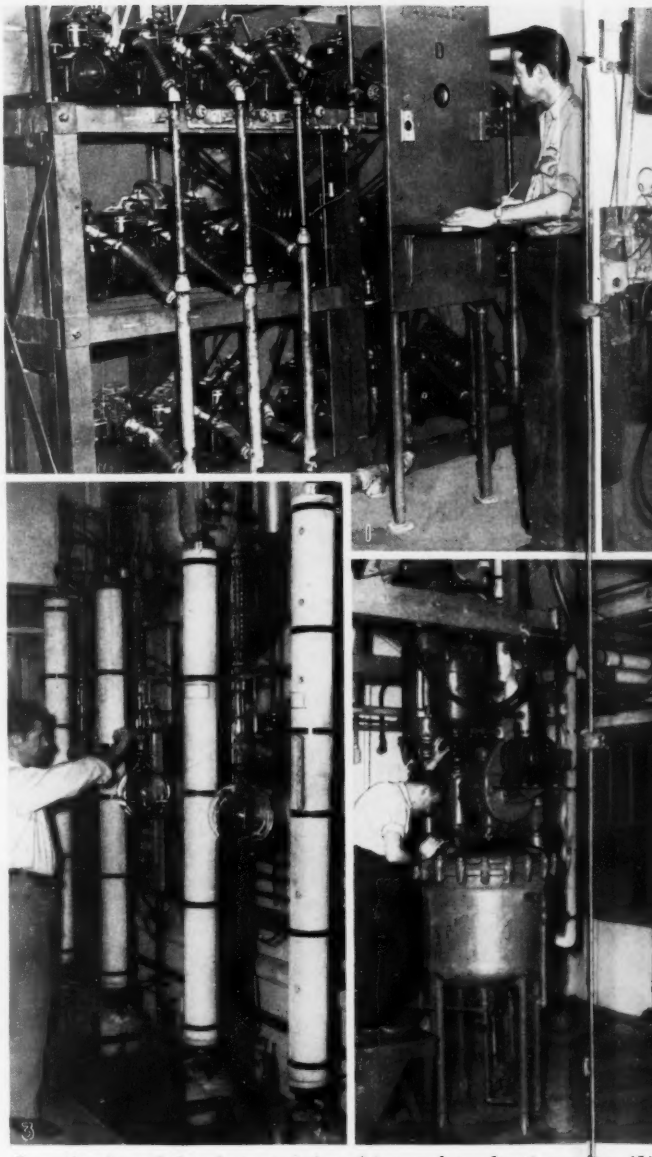
The Bureau contributed materially to the design and development of the test engines, equipment, and instrumentation now used to rate these fuels, and is at present conducting research directed toward improved test procedures. It also makes recommendations, based on analysis of data obtained by cooperating industrial laboratories, for the improvement of precision in testing. The petroleum industry is so large that even small errors can be enormously costly. For example, it has been estimated that an error of one octane number in rating motor gasolines, if made by all refiners, would cost them, and eventually the public, about a million dollars a day.

Reference Fuels for Knock Rating

Since the development of standardized engine tests in 1932, the National Bureau of Standards has served as the agency for the calibration of reference fuels such as normal heptane and isooctane used throughout the country for the knock rating of gasolines. Calibration is based on precise measurement of physical properties, on identification and estimation of impurities, and on careful comparisons of the fuels in a test engine with high-purity preparations of the same compounds. Acceptance of the sample depends on a check of the observed knock rating of the sample with a value calculated from the knock ratings of pure hydrocarbons. Specifications covering pertinent properties were prepared by the Bureau and have been adopted by the American Society for Testing Materials, the industrial standardizing agency for this work.

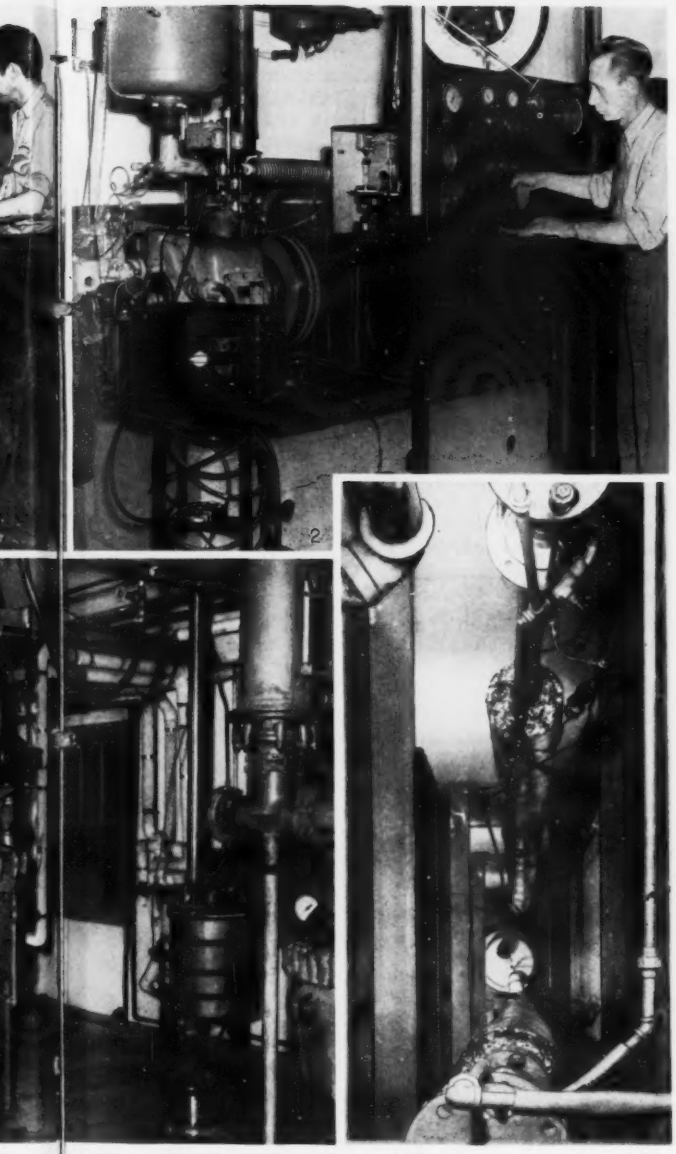
The Bureau's unique facilities have proved invaluable in this work in other ways. Some years ago it was noted that motor gasoline knock ratings made by laboratories located considerably above sea level did not agree with ratings made at sea level for the same gasolines. As early as 1937 a cooperative investigation clearly showed the effect of altitude upon ratings. Finally, in 1941, the Bureau was asked by the CFR Motor Fuels Division to assist in determining appropriate conditions for knock ratings by the ASTM Motor and CFR Research methods at elevations up to 7,000 feet. A series of cooperative tests was carried on in one of the Bureau's altitude chambers, utilizing skilled technicians and additional test engines made available by the participating organizations. As a result of this work, a new test procedure was adopted, making it possible for laboratories at altitudes up to about 10,000 feet to obtain results in agreement with those found by laboratories operating at sea level.

Later, when similar difficulties were experienced with the ASTM aviation-fuel test method, altitude studies were made at the Bureau to determine whether this procedure could also be corrected. However, as this method, unlike the ASTM motor-fuel method, is based on the evaluation of combustion chamber surface temperatures, it was not found possible to alter the procedure in such a manner as to give consistent results at all altitudes.



Investigation of the characteristics of internal combustion engines (1) synthesis and isolation of hydrocarbons (3, 4, 5) for use in high-knock the Bureau's automotive laboratory. Distillation apparatus (3), special columns (viewed from above, 5) are among equipment used in the pr

For a long time the octane number scale, developed in 1930 for use with motor fuels, also formed the basis for rating aviation fuels and their components. As long as none of these was better than isooctane, this scale was entirely satisfactory. Nearly a decade ago, how-



ion engines (1), calibration of reference fuels for knock testing (2), use in high-knock rating aviation fuels are representative of the work of ratus (3), specially designed reaction vessels (4), and 55-foot fractionation at used in the preparation of pure hydrocarbons.

ever, the quality of aviation fuels had so improved that some of them equalled isooctane in knock rating. As such fuels are a mixture of several hydrocarbons, it was not surprising that some of the components were found to be actually superior to isooctane. Ratings of these components were made provisionally in terms of the amount of tetraethyl lead that had to be added to raise the knock rating of isooctane to equal that of the pure hydrocarbon component.

This extension of the octane number scale was satisfactory for some years, but with the production of aviation fuels of ever higher octane number the limit of the scale was finally reached. Further addition of tetraethyl lead had little effect in improving the knock rating of isooctane, and it also caused erratic engine operation. The CFR Aviation Fuels Division therefore appointed a special committee, with the Bureau representative as chairman, to study the extension of the knock rating scale. The committee carried out a comprehensive program of exploratory research on reference fuel scales and on systems for expressing knock rating terms that would be of maximum usefulness. The Bureau contributed engine laboratory research and analyzed the test data submitted by other laboratories participating in the project. As a result of this work, the triptane-heptane reference fuel system and the Detonation Index rating scale have been recommended by the CFR Aviation Fuels Division for adoption.

Synthesis of Hydrocarbons

In 1934, the CFR Steering Committee requested the Bureau to make an investigation of the impurities present in primary standard reference fuels used in knock rating, with a view to developing specifications for the purity of these compounds. In the course of this work about 20 paraffin hydrocarbons were isolated as impurities in certified isooctane. As the total contamination that can be tolerated in such a reference fuel depends on the antiknock values of the constituents, it was necessary to determine not only the amount of each impurity present but also its knock rating. Several isooctane "impurities" were obtained in a state of higher purity than synthetic preparations made up to that time, and in the case of a few of these compounds the knock ratings exceeded that of isooctane—then considered the ultimate in knock rating.

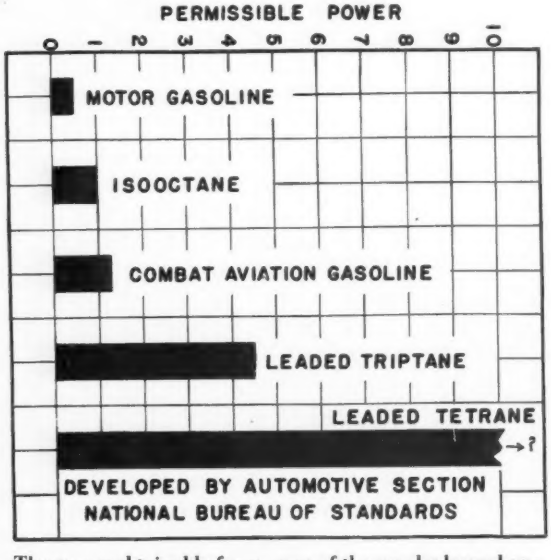
This work suggested the advisability of further research to determine what compounds and, more particularly, what types of compounds have higher knock ratings. In anticipation of the importance of such compounds as components of high-quality aviation gasoline in any future war, an investigation was begun in 1936 on the fuel properties of petroleum constituents. The objective of this program, sponsored by the National Advisory Committee for Aeronautics, the Army Air Corps, and the Navy Bureau of Aeronautics, was the synthesis of a suitably volatile aviation fuel having a knock rating, when used without tetraethyl lead, above that of isooctane. Individual hydrocarbons of the types found in petroleum were prepared in high purity, and their physical properties and combustion characteristics were ascertained. When the recent war began, the only accurate data available on the hydrocarbons, which later constituted the basis of our combat aviation gasoline, were those obtained in this research.

When this investigation was started, it was customary to prepare new hydrocarbons in quantities of from 10 to 200 ml. The synthesis of 10 gallons of a previously unsynthesized compound is a research problem

of the first magnitude. Such quantities of several hydrocarbons were needed, however, for comprehensive engine tests. As laboratory apparatus was not suited to these amounts, new equipment had to be developed. Among the first requirements were fractionating columns of higher efficiency and greater capacity than had been built at that time for laboratory use. Automatically operated fractionating columns, approximately twice the size of the largest laboratory distilling equipment then in use, were designed with many novel features, and they worked surprisingly well. Later, more satisfactory columns became available commercially. Large reaction kettles and superpressure equipment of special design were also needed in certain stages of the work.

In the course of time, synthetic hydrocarbon preparations began to issue from this laboratory in increasing volume. When the work was first undertaken, only a few of the triple-branched paraffins and one paraffin having four branches had ever been synthesized. Over 80 hydrocarbons have now been prepared in this laboratory, most of them in higher purity than in any previous preparation of these compounds. Many have a three- or four-branched carbon chain, and several have been obtained with five branches. A large proportion of these compounds had not previously been made.

In addition to the hydrocarbons that have been synthesized, a considerable number have been prepared in a pure state by fractionation of alkylates, polymers, and other mixtures which might be called "synthetic crudes." This has required fractionating columns of increasingly greater capacity and efficiency. When the work began, fractionating columns having a 4-liter pot and an 8-foot column were considered quite large. Later, however, when a new three-story building was being designed for the Bureau, provision was made for a shaft to house fractionating columns running from the basement to a penthouse on the roof. These 64-foot assemblies, operating at efficiencies of 150 to 200 theoretical plates, have pots of one-barrel capacity and columns 55 feet in effective height.



The power obtainable from some of the new hydrocarbons prepared at the Bureau, such as triptane and tetrane, greatly exceeds that provided by isooctane, the basis of the present octane number scale and a major constituent of aviation gasoline in World War II.

Samples of the highly purified compounds produced by synthesis and isolation of hydrocarbons are not only subjected to knock-rating tests to determine fuel quality, but are also furnished to laboratories for use as samples in the calibration of analytical instruments. Thus a project that began as a study of the impurities in one hydrocarbon has now become one of the largest sources of pure hydrocarbons.

In the latter part of the war, when the ever-increasing need for aviation gasoline put our productive capacity to its severest test, a study was made to determine whether any components usable in aviation gasoline could be extracted from the motor fuels then available for civilian use. The large fractionating columns were operated so as to simulate industrial superfractionation equipment. Analysis of a typical thermally cracked naphtha by this means showed regions of components that could add to the output of aviation gasoline. Although the war ended before these results could be applied, the equipment and technique are now available in the event of any future emergency.

Early in 1942, many of our oil tankers were being lost by enemy action, and it was becoming increasingly difficult to supply friendly nations with gasoline. In consequence, materials critically needed for the war effort could not be brought to seaports in those countries for shipping. A logical alternative to exporting gasoline was the encouragement of local production of substitute motor fuels. Under sponsorship of the Foreign Economic Administration, the automotive laboratory therefore undertook a comprehensive investigation of possible substitutes that could be produced from indigenous vegetation.

This investigation dealt with liquid, gaseous, and solid fuels. The phases of fuel behavior studied included starting under both sea level and altitude conditions, vapor lock, distribution, knock rating, power, economy, engine wear, and engine deposits. Such seemingly minor matters as the rate of evaporation and the life of fuel-pump diaphragms were also investigated. A major problem that arose was the adaptation of the McKee wear gage,[2] designed at the Bureau to measure wear in aircraft-engine cylinders, to use in automobile engines. It was demonstrated that complete-substitute motor fuels, containing no petroleum, could be prepared by either alcoholic or butyric fermentation. However, such fuels, although satisfactory in the moderate climates of eastern South America, would not be suitable in most of the United States, where large variations in local temperatures occur.

[2] See An indentation method for measuring wear, NBS Technical News Bulletin **31**, 75 (July 1947).

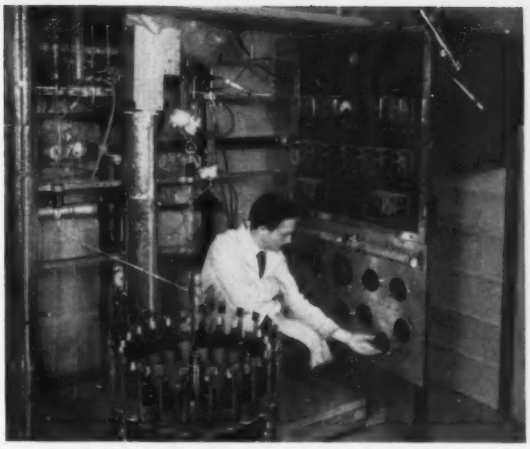
Engine Tests and Investigations

One of the major services of the Bureau to industry and to the public is the indirect one of making tests for and furnishing technical advice to other Government agencies in cases of alleged misrepresentation of products. Several hundred such cases have come to the automotive laboratory, largely from the Federal Trade Commission and the Post Office Department. Many of these concerned substances that had been advertised as improving motor performance when added to gasoline in small quantities—often in the form of tablets. In nearly all cases these tablets are naphthalene, of which moth balls are made. This substance as a gasoline additive is without effect on the power, economy, or performance of automotive engines. In fact, it has been found that no material, when added to gasoline in amounts of 1 percent (roughly 1 ounce per gallon) or less, will measurably increase the gasoline mileage, the ease of starting and warm-up, or the power if knock is not present. The saving to the public which has resulted from discouraging the manufacture and sale of such preparations is also of benefit to legitimate business.

During the war, the acute shortage of alcohols and glycol, normally used as the basis of automobile radiator antifreeze solutions, encouraged the production of substitute antifreezes. Most of these were either solutions of salts, such as calcium or magnesium chlorides, or were kerosene-like preparations made from petroleum. As it was known that salts when used as automotive antifreezes are highly corrosive, the Bureau and the automotive equipment and transportation industries called the attention of the War Production Board to this situation. After a series of tests in the automotive laboratory had again demonstrated the detrimental effects of salt- or petroleum-base antifreezes on cooling systems, the War Production Board prohibited the manufacture and sale of these preparations. The resultant saving of critical transportation equipment was of greater importance than the financial savings involved, as the production of war material at that time was highly dependent on the retention of available motor vehicles.

Since the War Production Board was dissolved, the continuing scarcity of standard types of antifreezes has led to resumption of the sale of both types of substitutes as permanent antifreezes. Although the Bureau has tested many salt antifreezes it has yet to find one, however inhibited, which is noncorrosive. The effects of petroleum-base antifreezes, if highly refined, have been found to be less serious than those of salt antifreezes. Detrimental action results from the petroleum dissolving the rubber out of ordinary radiator hose. The dissolved material tends to clog the radiator, and the hose is no longer liquid-tight. This disadvantage can be avoided by use of certain synthetic rubber hoses that are hydrocarbon-resistant. However, petroleum antifreezes also constitute a marked fire hazard in comparison with ethylene glycol antifreezes.

The extreme diversity of the test work of the automotive laboratory necessitates continual developmental research on test methods and equipment. Performance tests have been made on engines of all sizes, from those used in model aircraft and the 1-horsepower types used to power Army field generators and refrigerators, to 200-horsepower landing-boat engines.



The high purity of the hydrocarbons synthesized at the Bureau results primarily from the efficiency of automatic fractionating columns for final purification. Those above operate continuously throughout a distillation, with intermittent sampling (lower center) automatically timed by setting the control board.

In 1942 and 1943, at the request of the Army Ordnance Department, automotive engineers were detailed from the Bureau to assist in development tests of Army transport and combat vehicles. Field tests were conducted under high temperatures in the southern California desert as well as under subarctic conditions in northwest Canada. Design changes suggested in the course of this work contributed to the ability of these vehicles to function in the African campaign.

In the course of the war, a 20-cylinder German Diesel engine used in E-boats—the German equivalent of our PT-boats—was studied and its novel features evaluated. Tests were made on a battery-operated electric motor later used with notable success to drive torpedoes against Japanese shipping, and the explosion hazards involved in filling and repairing antisubmarine net-flotation buoys were investigated.

Current planning in automotive research at the Bureau lays emphasis on the study of jet fuel components, and on the investigation of methods for determination of combustion charactristics of fuels with a view to improving the precision of the present methods as well as the development of methods of greater significance. A new means of measuring wear on engine parts with a rapidity and precision hitherto unattainable is also under study. A beginning was made several years ago on the development of an automotive proving ground in cooperation with the Public Roads Administration, but the work was abandoned when the war began. Such a facility would be of great benefit not only to the Government but also to industry and the consumer.

Home-Plumbing Studies Use Plastic Pipe

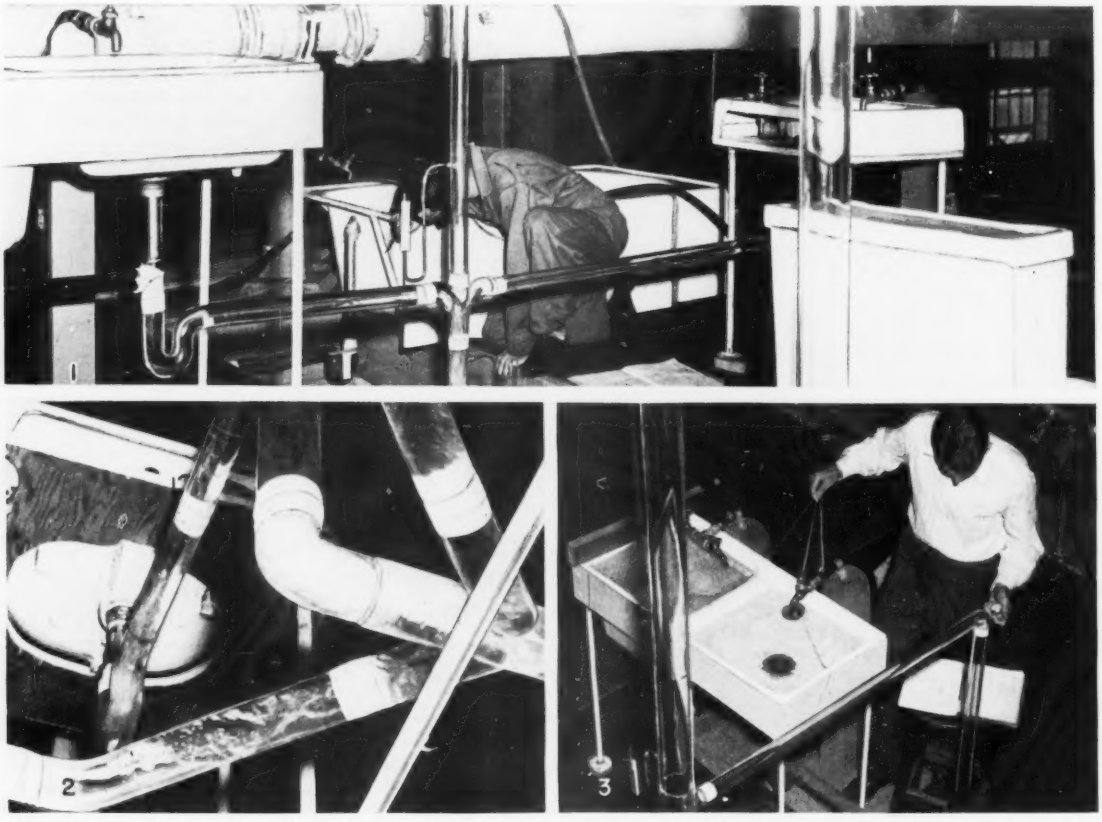
Hydraulic engineers at the Bureau are making a study of plumbing systems in which ordinary home plumbing is exactly duplicated except in one important respect—all of the pipes are made of plastic. The transparent pipes are being used so that investigators can see what is actually going on in a typical plumbing installation. This is supplemented with the data gathered from conventional pressure and water-level gages.

The research—directed at some of the more controversial plumbing problems—is being sponsored by the Housing and Home Finance Agency for the Uniform Plumbing Code Committee. Motion pictures are being made of the important tests so that local groups throughout the country can have visual facts to work with when plumbing code revision is under consideration.

Full-scale plumbing systems for two one-story houses and one two-story duplex have been erected. To complete the authenticity of the set-up, building and street sewers of conventional material were installed and means provided for loading the street sewer with a flow of up to 300 gallons per minute.

Three problems so far have occupied the investigators. They are (1) Self-siphonage; (2) stack venting; (3) wet venting. All three are problems connected with the proper venting of fixture traps.

Self-siphonage occurs when the length of the unvented waste pipe from the fixture—for example, the lavatory—is sufficiently long so that the water in the trap is pulled out by suction when the fixture is discharged. In plumbing drainage systems it is necessary to vent, in some manner, each fixture trap. The purpose of the vent is to keep pressures in the fixture drains sufficiently low so that the water seal in the fixture trap is not broken. Stack and wet venting are different methods of accomplishing this result. In stack venting the individual fixture wastes are led directly to the vertical stack, and the stack itself serves, under certain conditions, as a vent for the fixture attached to it. In wet venting, the drain from one



Full-scale plumbing systems of transparent plastic pipe enable NBS hydraulic engineers to see what is actually taking place in domestic plumbing installations. Systems for three different types of houses have been constructed, and the research is directed toward some of the basic problems encountered in plumbing design.

fixture serves as a vent for the trap of another fixture.

Each of the above problems is being investigated under many different conditions, involving various lengths, diameters, and slopes of fixture drains; various types of traps; and other variables.

That there has been no agreement among the experts in the field is attested to by the variance in plumbing code requirements in municipalities through the nation. It is expected that these investigations will establish facts that will be useful in leading the way to optimum conditions and requirements.

Directory of Commercial and College Laboratories

A complete listing of commercial and university testing and research laboratories throughout the country, together with indications of the type of commodities tested, has been compiled by the National Bureau of Standards. This pamphlet is now available from the Government Printing Office as NBS Miscellaneous Publication M187, entitled *Directory of Commercial and College Laboratories.*

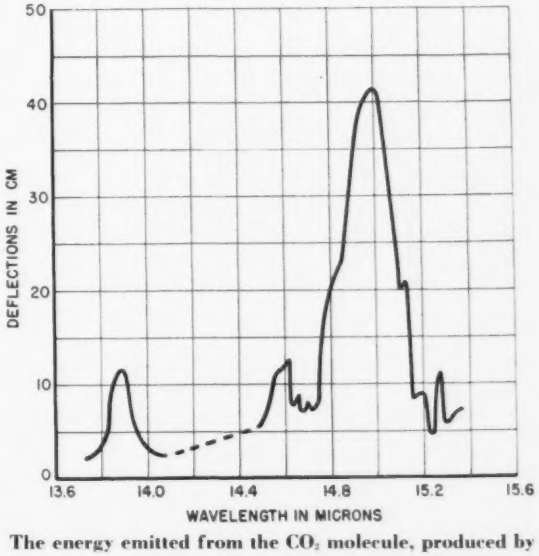
As the principal agency of the Federal Government for research and testing in physics, mathematics, chemistry, and engineering, the Bureau makes tests and carries out investigations for other Government organizations. However, it does not make tests for the general public if other laboratories can do the work with required accuracy. Because of the many inquiries regarding such service, this classified list of other testing facilities has been prepared. It is expected that the directory will also be of value to the large number of purchasers who are not equipped to make their own acceptance tests and have therefore hesitated to buy on specifications.

Information is given concerning 220 commercial laboratories, with 80 branches or offices, and 189 college laboratories used for research and testing, as well as instruction. Listings are arranged both geographically and alphabetically to facilitate the ready location of any laboratory. *Miscellaneous Publication M187 may be obtained only from the Superintendent of Documents, Washington 25, D. C., at 30 cents a copy.*

Infrared Radiation From Flames

The existence of certain emission bands in the infrared radiation from flames, first reported nearly fifty years ago but not confirmed in subsequent experiments by other investigators, has been demonstrated in recent studies by Dr. E. K. Plyler and associates in the Bureau's radiometry laboratory.

Nearly all the energy radiated from the Bunsen flame arises from transitions between the energy levels of the molecules of water vapor and carbon dioxide. In order to check the validity of various theories of combustion, it is highly desirable to know the relative amount of energy which is radiated during the different transitions. In Gaydon's book, "Spectroscopy and Combustion Theory," the suggestion is advanced that the energy radiated by the flame may arise from chemical processes rather than thermal processes. This suggestion is based, in part, on the uncertainty of the existence of certain emission bands in the 15μ region of the infrared spectrum which should be produced by allowed energy transitions of the CO_2 molecule. Many investigators have not been able to detect radiation in this region. Actually energy was observed in the infrared region of 15μ by Rubens and Aschkinass in 1898. They observed the energy from the Bunsen flame and also from heated carbon dioxide gas. Their studies on the emission of water vapor and CO_2 were of high quality, but because other workers failed to find sufficient energy for measurement in the 15μ region, their experimental data have not been fully accepted. In the work at the Bureau, the CO_2 radiation at 15μ has been detected in the Bunsen flame, confirming the observations of Rubens and Aschkinass, and it consists of two emission bands occurring at 14 and 15μ. These bands have been observed in the Bunsen flame while burning either manufactured or natural gas.



The energy emitted from the CO_2 molecule, produced by burning CO in air, is relatively intense in the region of 13.9 and 15.0μ, with a side band on the short wavelength side of the 15μ maximum. These regions of emission correspond to certain transitions between known energy levels of the CO_2 molecule.

In addition to the two emission bands of CO_2, there are a number of emission lines of water vapor. It would not have been possible to identify the CO_2 bands from the array of bands in the 15μ region if the emission of CO_2 had not been previously measured from the flame of burning CO in air. During the war Plyler

made the measurements of CO_2 radiation at the University of Michigan in connection with confidential industrial work. These results are now given for the first time. A grating with 1,200 lines per inch was used in the spectrometer and a KBr foreprism was used for separating the various orders. Two regions of the spectrum were found, 14 and 15μ, where the energy emitted by CO_2, produced by burning CO in the air, was relatively intense. The 15-μ maximum has a side band on the short wavelength side. These three regions of emitted energy correspond to the transitions between known energy levels of the CO_2 molecule. They are (10^00) to (01^10), (02^20) to (01^10), and (01^10) to (00^00). These transitions produce bands with frequencies of 721 cm^{-1}, 668 cm^{-1}, and 667 cm^{-1}. The transition, (10^00) to (01^10), shows that one of the energy levels of the inactive frequency of CO_2 changes at the same time as an active frequency, and radiation occurs. This inactive frequency may also lose energy by other transitions and collisions of the molecule with other molecules. Some energy was observed in the entire region from 13 to 17μ. However, the two strongest regions of radiation were observed at 14 and 15μ. There are other allowed transitions between energy levels which produce bands in this region. Also it may be possible to find a band at 647 cm^{-1} for the $C^{13}O_2^{16}$ molecule.

The question may be asked why were Rubens and Aschkinass able to observe this radiation of the CO_2 molecule at 15μ and, up to the present time, other observers could not. The answer is that Rubens and Aschkinass used a KCl prism, which does not absorb in the 15μ region. The absorption of a NaCl prism reduces the energy so much that it is difficult to detect the small amount of transmitted energy. Other observers could easily have observed the CO_2 radiation if they had used a KCl or KBr prism. This was discussed in a paper by Plyler, read before the Optical Society of America at Cincinnati in October. Slides were shown comparing the energy in the 15μ region as measured with NaCl and KBr prisms.

Additionall experimental data have been obtained which will be reported in a paper scheduled to appear in the February issue of the Journal of Research. These include certain bands which are attributed to hydrocarbons. In the region between 2.8 and 3.1μ, there were observed 15 rotational lines which were equally spaced and separated by 22 cm^{-1}. Many lines which are a part of the rotational spectrum of the H_2O molecule were also observed in the region between 12 and 24μ.

NBS Publications

Periodicals [3]

Journal of Research of the National Bureau of Standards, volume **39**, number 5, November 1947. (RP1835 to 1841, inclusive.)

Technical News Bulletin, volume **31**, number 11, November 1947. 10 cents.

CRPL–D38. Basic Radio Propagation Predictions for February 1948. Three months in advance. Issued November 1947.

Nonperiodicals

Research Papers [3,4]

RP1829. Influence of the atmosphere upon the precision of telescope pointing. Francis E. Washer and Leo W. Scott. 10 cents.

RP1830. Alkylbenzenes in the C_9 fraction from five different catalytic petroleum refining processes. Anton J. Streiff and Frederick D. Rossini. 10 cents.

RP1831. Heat capacities at high temperatures of uranium, uranium trichloride, and uranium tetrachloride. Defoe C. Ginnings and Robert J. Corruccini. 10 cents.

RP1832. Specific heat, enthalpy, and entropy of uranyl fluoride. Paul F. Wacker and Ruth K. Cheney. 5 cents.

RP1833. Purification, purity, and freezing points of *n*-decane, 4 alkylcyclopentanes, 9 alkylcyclohexanes, 2 monoolefins, 1,2-butadiene, and 2-butyne of the API-Standard and API-NBS series. Anton J. Streiff, Evelyn T. Murphy, Janice C. Zimmerman, Laurel F. Soule, Vincent A. Sedlak, Charles B. Willingham, and Frederick D. Rossini. 15 cents.

RP1834. Electrodeposition of tungsten alloys containing iron, nickel, and cobalt. Abner Brenner, Polly Burkhead, and Emma Seegmiller. 20 cents.

Building Materials and Structures Reports [3]

BMS 17–Supplement No. 2. Sound insulation of wall and floor constructions. 10 cents.

Commercial Standards [3]

CS17–47. Diamond core drill fittings. (Supersedes CS17–42.) 10 cents.

CS35–47. Hardwood plywood. (Supersedes CS35–42.) 10 cents.

CS129–47. Materials for safety wearing apparel. (Supersedes CS129–46.) 5 cents.

CS134–46. Cast aluminum cooking utensils (metal composition). 5 cents.

Simplified Practice Recommendations [3]

R17–47. Heavy forged hand tools (Supersedes R17–43.) 10 cents.

R45–47. Grinding wheels. (Supersedes R45–39.) 15 cents.

Miscellaneous [3]

M187. Directory of commercial and college laboratories. (Supersedes M171.) 30 cents.

Letter Circulars [5]

LC880. Porcelain and pottery: Publications by the staff of the National Bureau of Standards. (Supersedes LC762.)

LC881. Electrodeposition: Publications by the staff of the National Bureau of Standards. (Supersedes LC775.)

LC882. Revised classification of radio subjects used in National Bureau of Standards. (Supersedes LC814.)

LC883. List of Simplified Practice Recommendations. Revised to October 1, 1947. (Supersedes LC844.)

Articles by Bureau Staff Members in Outside Publications [6]

Rotary concentric-tube distilling column. C. B. Willingham, V. A. Sedlak, F. D. Rossini, and J. W. Westhaver. Ind. & Eng. Chem. (1155 Sixteenth St. NW, Washington 6, D. C.) **39**, 706 (1947).

The ionosphere. J. H. Dellinger. Scientific Monthly (1515 Massachusetts Ave. NW, Washington 5, D. C.) **65,** 115 (August 1947).

Elastic behavior and creep of refractory brick under tensile and compressive loads. Lewis E. Mong. J. Am. Ceramic Soc. (2525 North High Street, Columbus 2, Ohio) **30,** 69 (March 1947).

Properties of barium strontium titanate dielectrics. E. N. Bunting, G. R. Shelton, and A. S. Creamer. J. Am. Ceramic Soc. **30,** 114 (April 1947).

Surface tensions of some optical glasses. Leo Shartsis and Alden W. Smock. J. Am. Ceramic Soc. **30,** 130 (April 1947).

Tests for hot-water resistance of tank enamels. W. N. Harrison and D. G. Moore. J. Am. Ceramic Soc. **30,** 220 (July 1947).

Mechanism of thermal shock failure in enamelware: An oven test method. W. N. Harrison, J. C. Richmond, and A. C. Francisco. J. Am. Ceramic Soc. **30,** 227 (August 1947).

Investigations of plaster failure. E. S. Newman. Am. Ceramic Soc. Bul. (2525 North High Street, Columbus 2, Ohio) **26,** 117 (April 15, 1947).

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[3] Send orders for publications under this heading only to the Superintendent of Documents, Government Printing Office, Washington 25, D. C. Annual subscription rates: Journal of Research, $4.50 (foreign $5.50); Technical News Bulletin, $1.00 (foreign $1.35); Basic Radio Propagation Predictions, $1.00 (foreign $1.25). Single copy prices of publications are indicated in the lists.

[4] Reprints from October Journal of Research.

[5] Available on request from the National Bureau of Standards, Washington 25, D. C. Letter Circulars are prepared to answer specific inquiries addressed to the Bureau, and are sent only on request to persons having a definite need for the information. The Bureau cannot undertake to supply lists or complete sets of Letter Circulars or send copies automatically as issued.

[6] These publications are not available from the Government. Requests should be sent direct to the publishers.

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